Development Of Non-chemically Amplified Photoresists for Extreme Ultraviolet (EUV) Lithography

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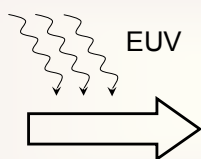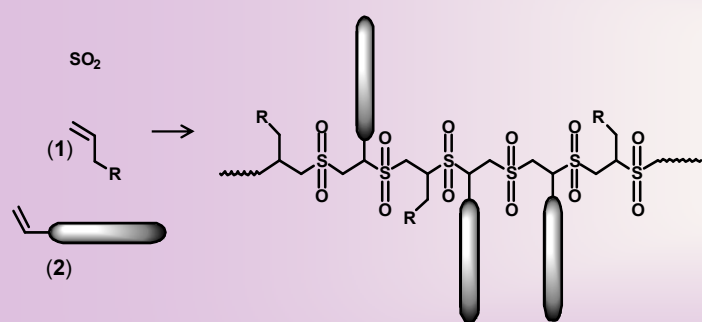
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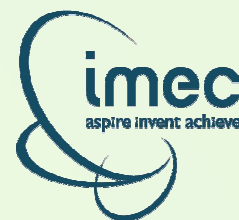
INTRODUCTION

Current photoresist technologies rely heavily on the use of photoacid generators (PAG) to chemically amplify the response of the resist formulation to the incident radiation. However, the diffusive path length of the protons (and counter-ion) generated by the PAG is significant compared with the target dimensions of EUV lithography. Additionally, the problem of low sensitivity, and hence increased production costs, is encountered when alternatives to photo-acid generation are used to produce chemical changes. Thus, the objective of this investigation is to develop new polymeric non-chemically amplified materials having higher sensitivity, for use as photoresists in EUV lithography.

Poly(olefin sulfones)
★ Polymers formed by the reaction of sulfur dioxide (SO_2) and olefins which are highly sensitive to degradation by EUV radiation[1]
★ Exhibit low ceiling temperatures (T_c) and have propensity to 'unzip' to parent monomers following scission of C-S backbone bonds
★ Main-chain scission unzipping mechanism removes the need for chemical amplification
★ Possible to terpolymerise third macromonomer to tailor desired attributes to resist material e.g. adhesion promotion, etch resistance, high T_g
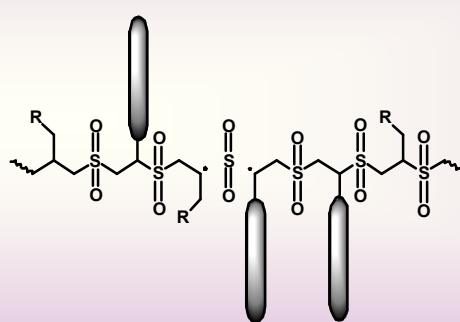
AIMS

★ To synthesise and characterise a range of sulfone terpolymers containing PMMA side arms
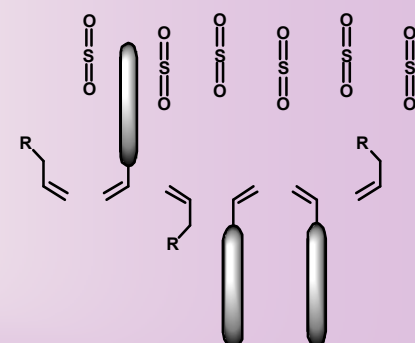★ Evaluate the effect of side arm length and incorporation density on EUV lithographic performance

Resist Synthesis   **Resist Irradiation**   **Post Exposure Bake**

SO_2 (1)   EUV   Δ

(1) – 1-pentene
(2) – Macromonomer which can be tailored to suit desired properties of resist e.g. High T_g, Adhesion Promotion, Etch Resistance

SYNTHETIC METHODOLOGIES AND RESULTS

Resist Synthesis

Cu(I)Br
Toluene, 90°C

n = 27 (1)
n = 48 (2)
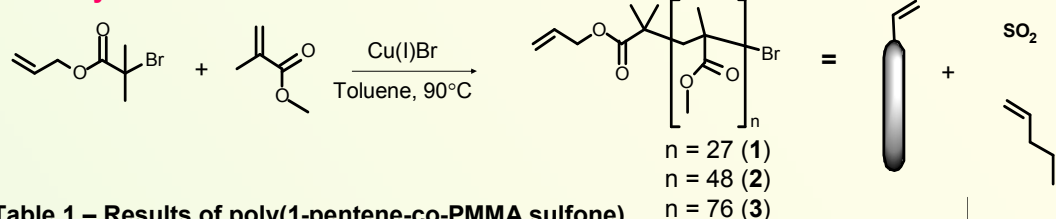n = 76 (3)

SO_2
t-BuOOH
-78°C

(4a-e)

Table 1 – Results of poly(1-pentene-co-PMMA sulfone) synthesis (4)

PMMA macromonomer M_n (Da)	No. % PMMA in product^	Wt. % PMMA in product	M_n* (Da)	PDI	T_g (°C)
-	-	-	47k	2.4	84.5
2.7k (1)	0.16	1.0	83k	2.2	84.5
	0.43	7.0	90k	2.1	84
	0.87	23	130k	1.7	84
4.8k (2)	1.0	42	47k	3.4	85
7.6k (3)	0.60	29	39k	2.6	84

*Obtained using triple detection on a DMAC GPC system. ^ Found using ^1H NMR.

EUV Outgassing – Degradation Products

★ All materials shown to degrade cleanly to 1-pentene and SO_2
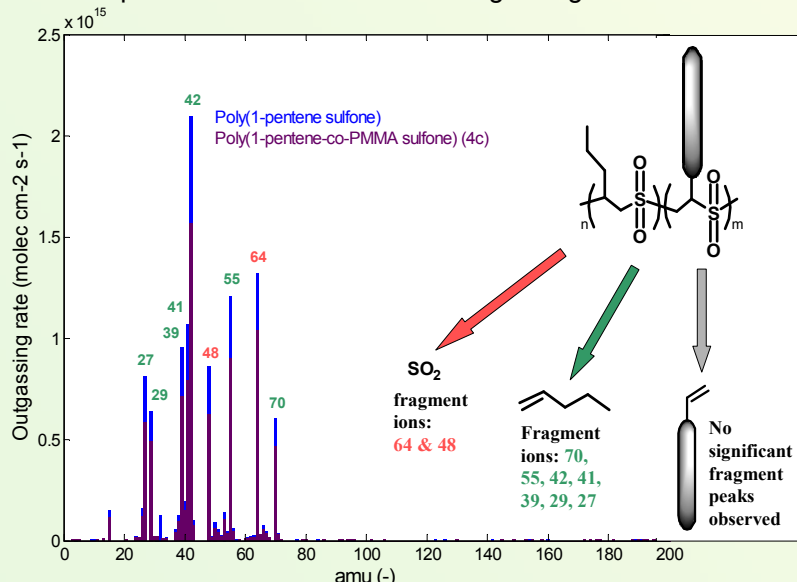★ Incorporation of PMMA reduces outgassing

Figure 1 - Outgassing species from poly(1-pentene sulfone) and poly(1-pentene-co-PMMA sulfone) containing 23 wt% 2.7k PMMA

EUV Outgassing - Witness Plate Contamination

★ High levels of outgassing
★ Witness plate contamination found to be low compared to some CAR materials and independent of outgassing rate

Table 2 – Outgassing and contamination properties

Resist	Outgassing Rate (mol cm^{-2} s^{-1})*	Total Outgassing (mol cm^{-2})*	Witness Plate Contamination (a.u.)*^
Poly(1-pentene sulfone)	4.67×10^{15}	1.94×10^{17}	2.96
	1.08×10^{16} #	8.38×10^{16}	0.37
Poly(1-pentene-co-PMMA sulfone) (4c)	3.52×10^{15} (-24%)	1.52×10^{17} (-21%)	not tested
Resist A§	1.54×10^{14}	2.75×10^{14}	<0.02
Resist B	3.07×10^{14}	4.68×10^{14}	0.3

*Dose 80 x E0. #Dose 10 x E0. ^Based on thickness (nm) difference measured by ellipsometry between background and resist exposure sites on witness plate, and normalised to exposed resist area. §ADT approved material.
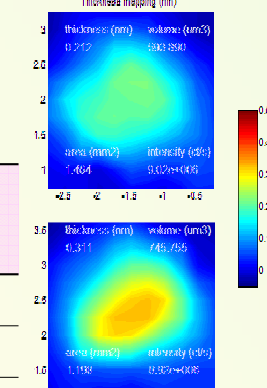

Figure 2 - Example of thickness measurement by ellipsometry over background (top) and poly(1-pentene sulfone) resist (bottom) contaminated areas of the witness plate.

EUV Patterning

★ Initial patterning studies show 35nm patterning in poly(1-pentene sulfone) possible
★ E_{size} = 70mJ/cm² for 50nm hp and 90mJ/cm² for 35nm hp
★ Optimisation of patterning parameters expected to lower achievable cd

50nm hp cd = 49.6 nm   35nm hp cd = 37.6 nm
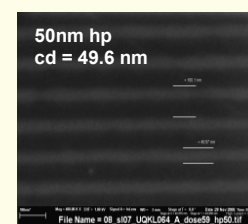
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Figure 3 - Lines patterned into poly(1-pentene sulfone) at 50nm and 35nm half pitches using EUV interference lithography.

CONCLUSIONS

★ Synthesis of a range of poly(1-pentene-co-PMMA) terpolymers achieved
★ Incorporation of PMMA macromonomer shown to reduce outgassing
★ Despite high levels of outgassing, witness plate contamination comparable to some commercial materials
★ Patterning of 35 nm hp lines achieved

REFERENCES

(1) Jack, K.; Blakey, I.; Hill, D.; Wang, Y.; Cao, H.; Leeson, M.; Denbeaux, G.; Waterman, J.; Whittaker, A. Proceedings of SPIE-The International Society for Optical Engineering 2007, 6519.

ACKNOWLEDGEMENTS